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ARYLIDENE POLYMERS. II.* SYNTHESIS AND CHARACTERIZATION OF SOME NEW POLYESTERS OF DIARYLIDENECYCLOPENTANONE

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ABSTRACT

New polyesters formed by interfacial polycondensation of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (II) with 4,4'-diphenic, isophthaloyl, terephthaloyl, adipoyl, suberoyl, and sebacoyl dichlorides were obtained. The yield and the values of the reduced viscosity of the produced polyesters were found to be affected by the type of organic phase, the quantitative ratio of organic to aqueous phase, the concentration of the hydrogen chloride acceptor, and the contribution of benzyltriethylammonium chloride as a catalyst. In order to characterize these polymers, the necessary model compounds were prepared from I, II, and benzoyl chloride. The resulting polyesters were confirmed by IR, elemental analysis, viscometry, DTA, DSC measurements, and thermogravimetric analysis. The crystallinities of all polyesters were examined by x-ray analysis, and the electrical properties of the polyesters were tested.

INTRODUCTION

Unsaturated polyesters have interesting applications such as for reinforcing [1, 2], chemical, thermally resistant, and self-extinguishing materials. A literature survey

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reveals that unsaturated polyesters can be synthesized by the condensation of a dihydric alcohol with an unsaturated acid [3]. Ponnusamy et al. [4] prepared and studied some unsaturated copolyesters based on the interaction of unsaturated diols with saturated acids. Recently, an unsaturated polyester was synthesized by interfacial polycondensation of 2,6-di(4-hydroxystyryl) pyridine with terephthaloyl or adipoyl [5].

The present investigation deals with the synthesis and characterization of some new diarylidene cyclopentanones based on aromatic and aliphatic polyesters. Interest is focused on the optimum preparation conditions. Their crystallinity, thermal stability, and electrical properties were also examined.

EXPERIMENTAL

Measurements

Elemental analyses were done on a Perkin-Elmer 240C instrument. The IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer by using the KBr pellet technique. Proton NMR spectra were run on a Varian EM-390-90 MHz NMR spectrometer at room temperature in CDCl_3 or DMSO using TMS as the internal reference. The inherent viscosities of a polymer solution (0.5% w/v) in DMSO were determined at 30°C by using an Ubbelohde suspended level visometer. The solubilities of polymers were examined by using 0.02 g polymer in 3–5 mL solvent at room temperature. X-ray diffractographs were obtained with a Philips x-ray PW 1710 diffractometer using Ni-filtered CuK_α . Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in air with Du Pont 951, 910, and 1090 thermal analyzers at a heating rate of 10°C/min. Pellets for electrical conductivity measurements were pressed at a constant 1000 psi with an IR die. Silver paste was used to make the contacts and the sample was sandwiched between two graphite electrodes. Conductivities were measured at room temperature in air with a 610C Keithley electrometer.

Reagents and Materials

4,4-Diphenic dichloride was prepared according to the literature [6] and recrystallized twice from tetrachloromethane (mp 185°C). Terephthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (mp 83–84°C). Isophthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (mp 44°C). Adipoyl, suberoyl, and sebacoyl dichlorides [7] were freshly distilled: adipoyl dichloride at 125°C/11 torr, suberoyl dichloride at 150°C/12 torr, and sebacoyl dichloride at 182°C/16 torr were used. Sodium hydroxide was of analytical grade. All other chemicals were of high purity and were further purified by standard methods [8].

Monomer Synthesis

2,5-Bis(4-hydroxybenzylidene)cyclopentanone (I)

A mixture of 0.2 mol *p*-hydroxybenzaldehyde and 0.1 mol cyclopentanone was dissolved in 100 mL ethanol at 50°C. The warmed reaction mixture was stirred while dry hydrogen chloride gas was introduced as a catalyst. After 2 h of stirring, a solid product separated out. The solid material was filtered off, washed with several portions of water, dried, and recrystallized twice from dioxane. Yellow needles were obtained; yield 89%, mp 332°C (literature [9]: 331°C).

Analysis. Calculated for C₁₉H₁₆O₃: C, 78.08; H, 5.48%. Found: C, 77.93; H, 5.43%. IR (KBr): at 1580 cm⁻¹ (s, C=C), at 1690 cm⁻¹ (s, C=O), at 3450–3470 cm⁻¹ (br OH). ¹H-NMR (δ/DMSO), at 9.8 (s, 2H, 2OH), at 7.5 (m, 2H of 2CH=C), 7.10–7.45 (m, 8H of Ar-H), at 3.3 (s, 4H of 2CH₂ cyclopentanone) ppm.

2,5-Bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (II)

This compound was prepared as described in previous methods, and recrystallized twice from methanol as yellow plate crystals: yield 92%, mp 215°C (literature [9]: 215°C).

Analysis. Calculated for C₂₁H₂₀O₅: C, 70.39; H, 5.59%. Found: C, 70.32; H, 5.53%. IR (KBr): at 1610 cm⁻¹ (s, C=C), at 1590 cm⁻¹ (s, C=O), at 2445–3450 cm⁻¹ (br, OH). ¹H-NMR (δ/CDCl₃), at 9.7 (s, 2H, of 2OH), at 7.95 (m, 2H of CH=C), at 7.15–7.35 (m, 6H, Ar-H), at 3.85 (s, 6H, 2OCH₃), at 3.15 (s, 4H, 2CH₂ of cyclopentanone) ppm.

Synthesis of Model Compounds A and B

General Procedure

2,5-Bis(4-hydroxybenzylidene)cyclopentanone or 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (5 mmol) was dissolved in 20 mL sodium hydroxide solution (10 mmol) and stirred at 25°C. After stirring, benzoyl chloride (10 mmol) was carefully added within 20 min. At the end of the reaction time, a highly yellow solid precipitated. The solid product was filtered off, washed with water, dried *in vacuo* at room temperature, and recrystallized from an appropriate solvent.

2,5-Bis(4-hydroxybenzylidene)cyclopentanone Dibenzoate (A)

An analytical sample was obtained by recrystallization from benzene; mp 240°C, yield 95%.

Analysis. Calculated for C₃₃H₂₄O₅: C, 79.20; H, 4.80%. Found: C, 79.14; H, 4.73%. IR (KBr): at 1750 cm⁻¹ (s, C=O of ester group), at 1690 cm⁻¹ (s, C=O of cyclo-

pentanone), at 1580 cm^{-1} (s, C=C group). $^1\text{H-NMR}$ (δ/CDCl_3) at 8.15(m, 2H, CH=C), at 7.45–7.65 (m, 10H, Ar-H ester), at 7.25–7.35 (m, 8H, Ar-H benzylidene), at 3.15 (s, 4H, 2CH_2 of cyclopentanone) ppm.

2,5-Bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone Dibenzoate (B)

A pure sample was obtained by recrystallization from benzene; mp 210°C , yield 89%.

Analysis. Calculated for $\text{C}_{35}\text{H}_{28}\text{O}_7$: C, 75.00; H, 5.00%. Found: C, 74.92; H, 5.08%. IR (KBr): at 1750 cm^{-1} (s, C=O of ester group), at 1690 cm^{-1} (s, C=O of cyclopentanone), at 1590 cm^{-1} (s, C=C group). $^1\text{H-NMR}$ (δ/CDCl_3) at 8.2 (m, 2H, CH=C), at 7.25–7.65 (m, 10H, Ar-H ester), at 6.95–7.25 (m, 6H, Ar-H), at 3.7 (s, 6H, 2OCH_3), at 3.15 (s, 4H, 2CH_2 of cyclopentanone) ppm.

Synthesis of Polyesters

A three-necked flask, equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet, and dropper, was charged with a mixture of 0.01 mol diarylidene cyclopentanone (I or II), 25 mL methylene chloride, and a suitable quantity of sodium hydroxide. A stoichiometric quantity (0.02 mol) or 100% excess (0.04 mol) of the latter dissolved in 100 mL water was also introduced. After mixing, 0.01 mol of acid chloride (III_{a-c}) dissolved in 25 mL methylene chloride was added over a 2-min period at 25°C and vigorously stirred. After complete addition of acid chloride, stirring was continued for 60 min whereby a highly-yellowish solid separated out. The solid was filtered off; washed with water, hot alcohol, and hot acetone; and dried under reduced pressure (1 mmHg) at 100°C for 2 days.

The synthesized polyesters, their yields, and some of their properties are listed in Table 1.

RESULTS AND DISCUSSION

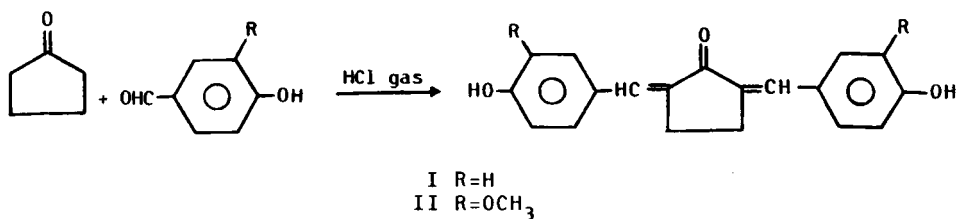
The preparation of polyesters was based on 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) or 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (II). The monomeric unit was synthesized by the condensation of 2 moles of 4-hydroxybenzaldehyde or 4-hydroxy-3-methoxybenzaldehyde with 1 mole of cyclopentanone in the presence of ethanol and a catalytic amount of dry HCl (Scheme 1).

Because the interfacial polycondensation in the presence or absence of benzyltriethylammonium chloride (BTC) is known to be useful for the synthesis of general aromatic polyesters and their analogs [10–12], this method was applied for the preparation of some new polyesters containing dibenzylidenecyclopentanone moiety as shown in Scheme 2.

TABLE 1. Elementary Analysis, Reduced Viscosity, Yield, and Electrical Properties of Polyesters IV_{a-f} and V_{a-f}

Polymer no.	Analysis						Yield, %	η_{red}^b dl/g ^a	Electrical conductivity, ohm-cm ⁻¹
	C, %		H, %		Found	Calcd			
	Calcd	Found	Calcd	Found					
IV _a	79.51	79.23	4.42	4.38	89.2	—	2.1 × 10 ⁻¹⁴		
IV _b	76.78	76.51	4.27	4.19	92.3	—	3.5 × 10 ⁻¹⁴		
IV _c	76.78	76.62	4.27	4.23	93.3	—	2.7 × 10 ⁻¹⁴		
IV _d	74.63	74.45	5.47	5.39	95.3	0.73	3.4 × 10 ⁻¹⁴		
IV _e	75.30	75.19	6.05	5.98	93.8	0.65	2.2 × 10 ⁻¹⁴		
IV _f	75.98	75.79	6.55	6.49	89.5	0.83	3.3 × 10 ⁻¹⁵		
V _a	75.27	75.11	4.65	4.51	94.1	—	2.9 × 10 ⁻¹³		
V _b	72.20	72.03	4.56	4.47	90.8	—	3.4 × 10 ⁻¹³		
V _c	72.20	72.11	4.56	4.51	94.7	—	2.8 × 10 ⁻¹³		
V _d	70.13	69.93	5.63	5.48	83.8	0.89	3.6 × 10 ⁻¹³		
V _e	71.02	70.89	6.12	5.99	96.3	0.64	1.9 × 10 ⁻¹⁴		
V _f	71.81	71.64	6.56	6.49	91.9	0.92	3.5 × 10 ⁻¹³		

^aReduced viscosity measured in DMSO at 30°C.



SCHEME 1.

To determine the optimum conditions in the interfacial polycondensation of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (II) with 4,4'-diphenic, isophthaloyl, terephthaloyl, adipoyl, suberoyl, and sebacoyl dichlorides (II_n), poly[oxysebacoyloxy-*p*-phenylenemethyldiyne (2-oxo-1,3-cyclopentanediyldiene)methylidyne-*p*-phenylene] (IV₁) was chosen as the model system. For the choice of optimum conditions, the yield of the process and the value of the reduced viscosity were considered. The effect of the following parameters were studied: the kind of organic phase, the quantitative ratio of organic to aqueous phase, the concentration of hydrogen chloride acceptor, and the contribution of benzyltriethylammonium chloride as a phase-transfer catalyst.

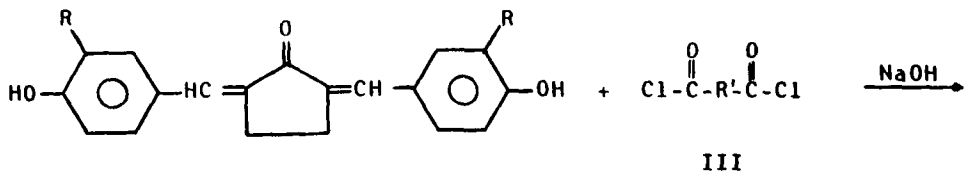
The organic phases used in the polymerization were tetrachloromethane, chloroform, and methylene chloride. Polyesters of the highest yield and reduced viscosity were produced with methylene chloride (Table 2).

The influence of the ratio of the aqueous to organic phase (1:1), which corresponds to the concentration of I in the aqueous-basic phase (0.1–1 mol/L) was examined. Figure 1 shows that the highest value of reduced viscosity and the best yield were obtained from a 0.1-*M* solution of I. The amount of NaOH used as a hydrogen chloride acceptor exerts considerable influence on the results of polycondensation (Fig. 2). The use of a quantity of benzyltriethylammonium chloride equal to 10% of

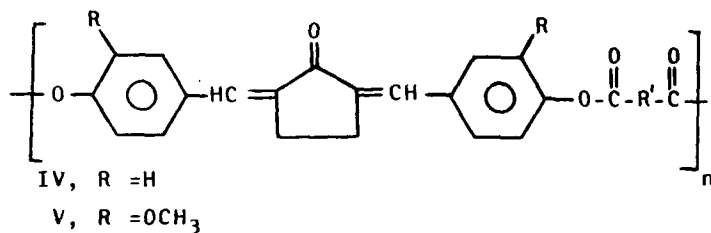
TABLE 2. The Organic Phase Effect on the Yield and Reduced Viscosity of Polyester IV₁^a

Organic phase	Yield, %	η_{red} , dL/g
Tetrachloromethane	89.6	0.73
Chloroform	90.1	0.84
Methylene chloride	99.3	0.98

^aConditions of the reaction: reagent ratio, 1:1; time of acid chloride addition, 2 min; temperature, 25°C.



I, R = H
 II, R = OCH₃



III	III _a ,	III _b ,	III _c ,	III _d ,	III _e ,	III _f
-R'-	<p style="text-align: center;">a</p>		<p style="text-align: center;">b</p>		<p style="text-align: center;">c</p>	
	$-(\text{CH}_2)_4-$		$-(\text{CH}_2)_6-$		$-(\text{CH}_2)_8-$	
	d	e	f			

SCHEME 2.

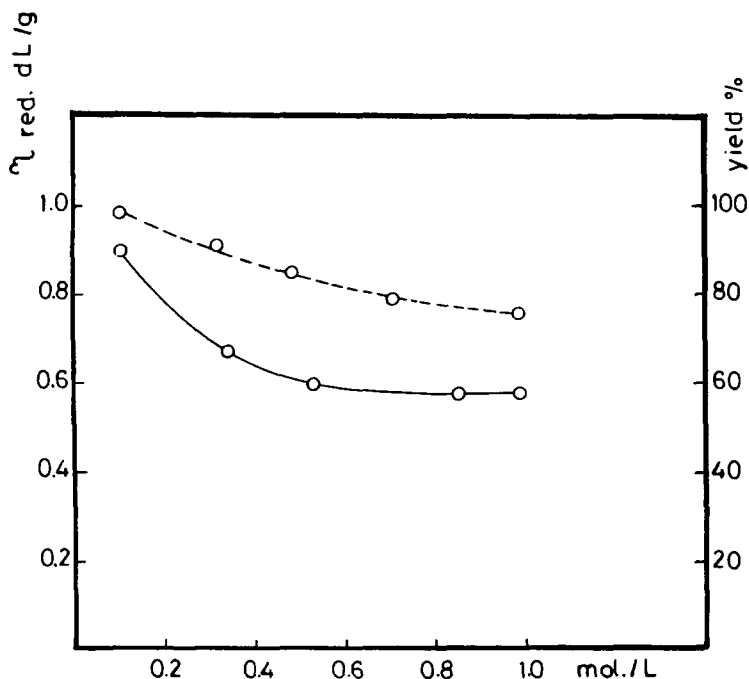


FIG. 1. The effect of 2,5-bis(4-hydroxybenzylidene)cyclopentanone concentration on yield (---) and reduced viscosity (—) of polyester IV_f. Organic phase, methylene chloride; 100% excess of NaOH; time of acid chloride addition, 2 min; temperature, 25°C.

the weight of I increased the value of the yield and the reduced viscosity of the polyester with and without a 100% excess of sodium hydroxide, as shown in Table 3.

To characterize the polyesters, model compounds A or B were prepared by the interaction of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (II), respectively, and benzoyl chloride in sodium hydroxide solution. Based on good agreement between calculated and found analytical data, IR, and NMR, these reactions are illustrated as shown in Scheme 3.

The resulting polyesters were characterized by IR spectroscopy, elemental analysis, solubility, viscometry, DSC, DTA measurements, thermogravimetric, and x-ray analysis. The electrical properties of all the polyesters were also tested.

The IR spectra of all the polyesters showed the disappearance of characteristic absorption band of the OH group and the appearance of the C=O of ester groups at

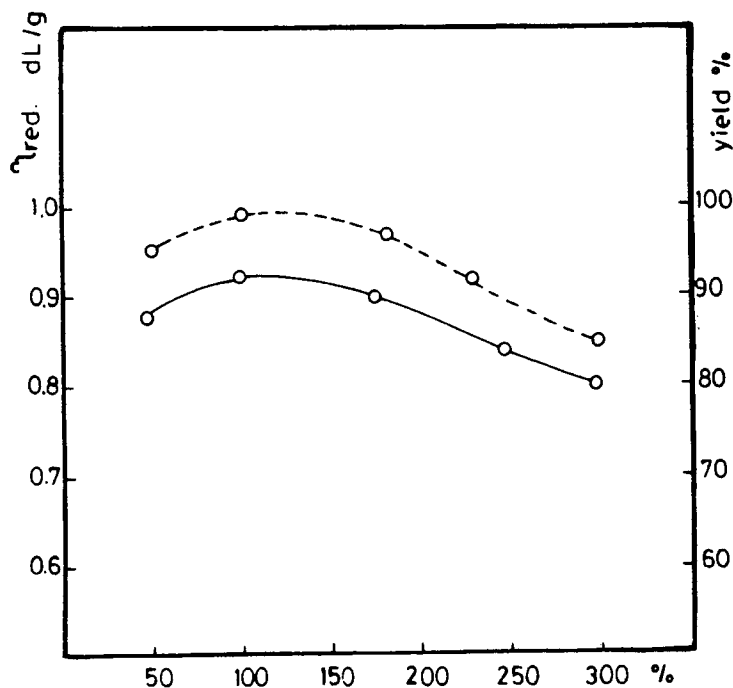
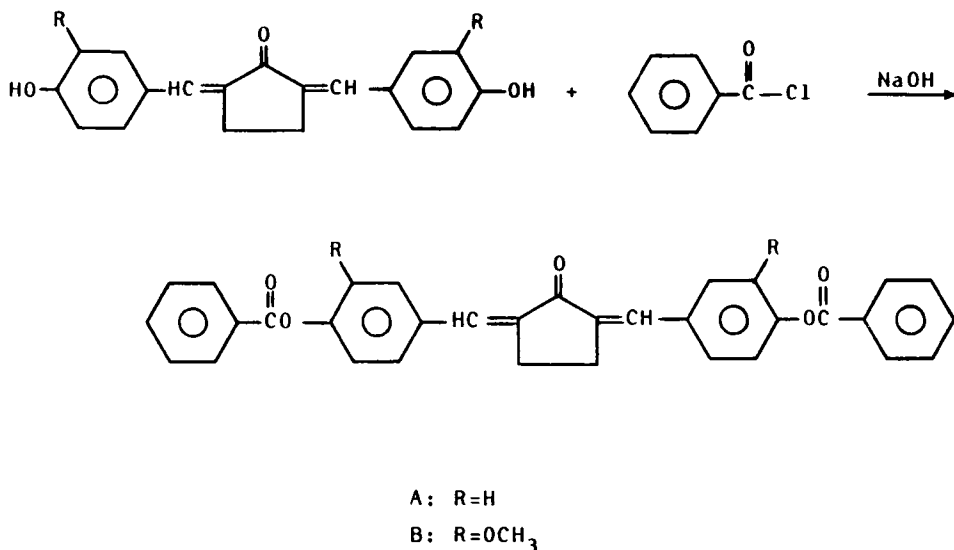


FIG. 2. The effect of an excess of hydrogen chloride acceptor (NaOH) on yield (---) and reduced viscosity (—) of polyester IV_f. Organic phase, methylene chloride; time of acid chloride addition, 2 min; phase ratio, 1:1; temperature, 25°C.

TABLE 3. The Effect of BTC on the Yield and Reduced Viscosity of Polyester IV_f^a

100% excess NaOH	Catalyst	Yield, %	η_{red} , dL/g
-	-	90.2	0.48
-	+	92.1	0.55
+	-	95.4	0.62
+	+	98.1	0.93

^aConditions of the reaction: reagent ratio, 1:1; time of acid chloride addition, 2 min; temperature, 25°C.



SCHEME 3.

1745–1755 cm^{-1} , at 1680–1695 cm^{-1} for the C=O of cyclopentanone, at 1580–1600 cm^{-1} for C=C groups, and the other characteristic absorption bands for the rest of the molecule.

Polymers IV_{a-f} and V_{a-f} were insoluble in DMF, NMP, phenols, cresols, and a phenol-CCl₄ mixture. They were slightly soluble in DMSO, except that Polymer IV_f was freely soluble in DMSO. In strong solvents like trifluoroacetic acid, methanesulfonic acid, and sulfuric acid, the polymers are completely soluble (concentrated H₂SO₄ gave a reddish-violet color). The slightly higher solubility of aliphatic polyesters IV_{d-f} and V_{d-f} in DMSO in comparison with that (2%) of the corresponding polyesters-based aromatic IV_{a-d} and V_{a-d} showed that the presence of aliphatic chain with four, six, or eight methylene groups in the rigid benzene position causes only a small increase in solubility.

X-ray diffractograms of the polyesters-based aromatic IV_{a-d} and V_{a-d} (Figs. 3 and 4) showed amorphous halo patterns in the $2\theta = 5\text{--}35^\circ$ region, and this indicated a low degree of crystallinity. Aliphatic polyesters IV_{e-f} and V_{e-f} (Figs. 3 and 4) showed a few reflections of sharpness peaks intermediate between crystalline and amorphous interference, and this indicated a high degree of crystallinity. It is noted that the presence of four, six, and eight methylene groups in polyesters IV_{e-f} and V_{e-f} increases polymer chain flexibility, and that might be responsible for the approach and mutual attractions of adjacent chains and thus induce crystallinity [13].

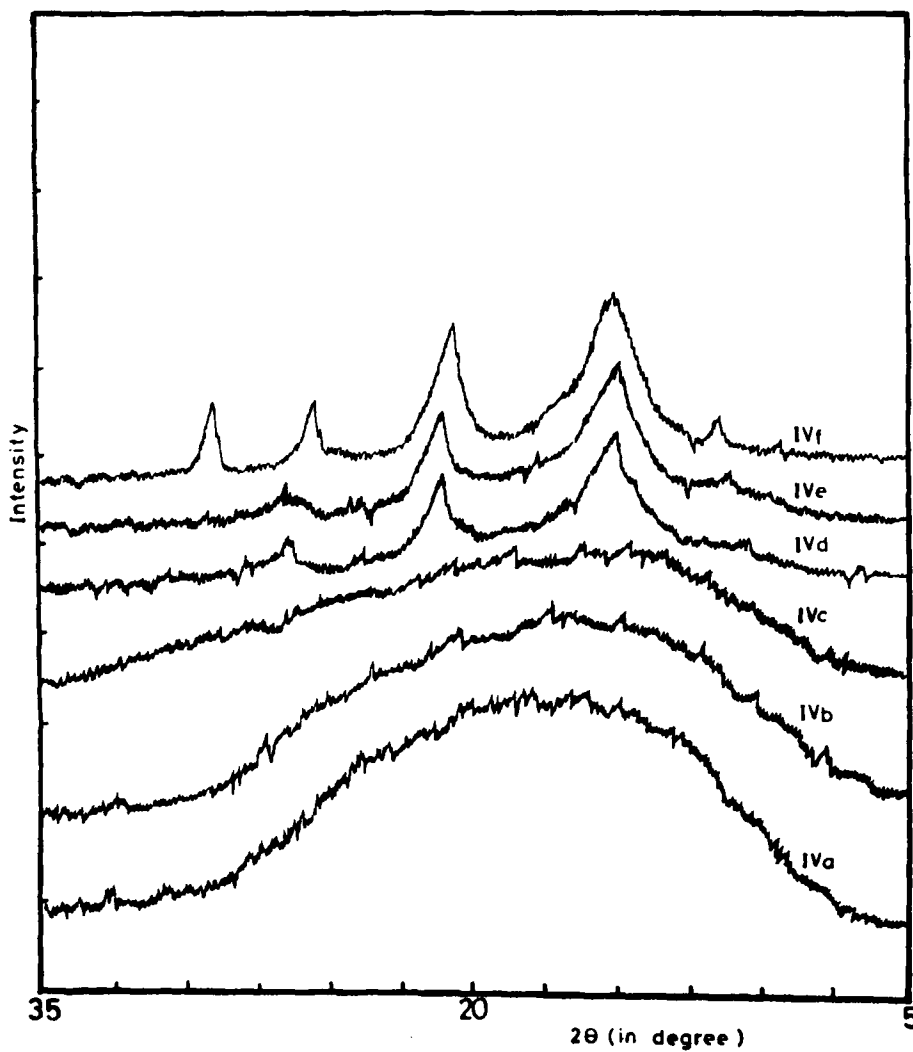


FIG. 3. X-ray diffraction patterns of polyesters IV_{a-f}.

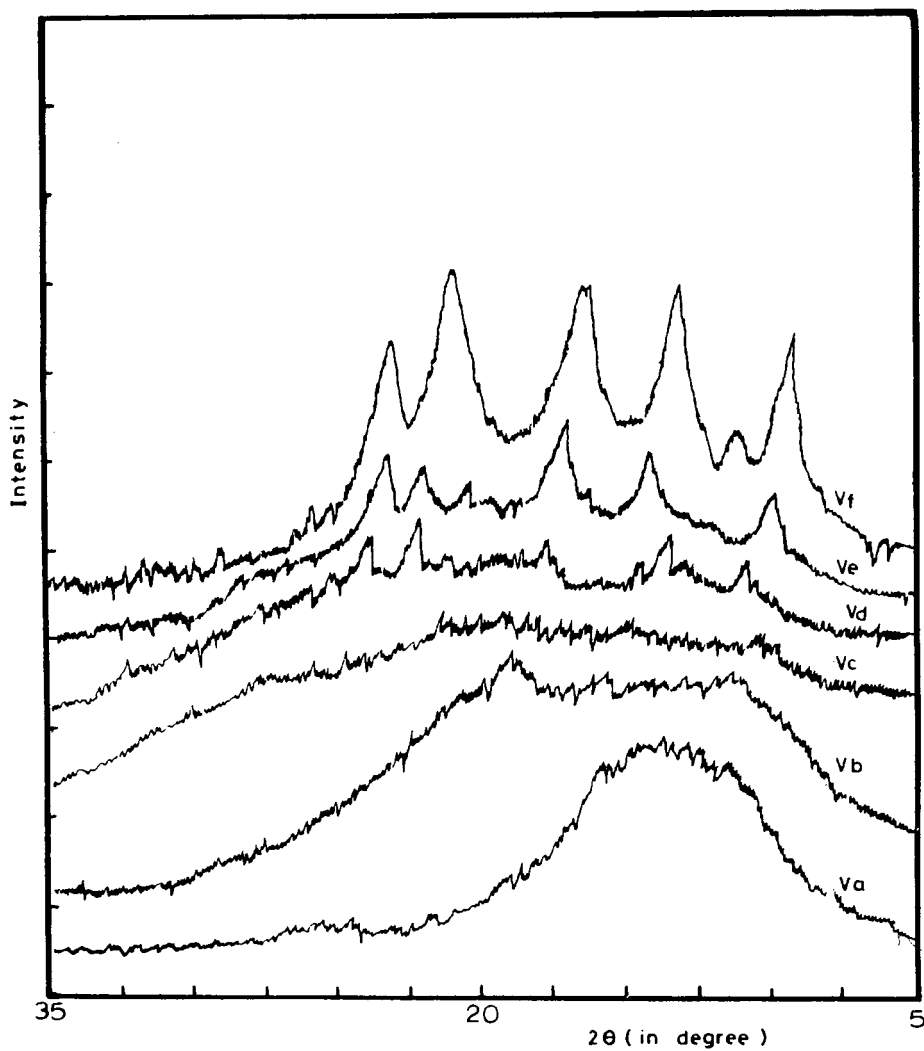


FIG. 4. X-ray diffraction patterns of polyesters V_{a-f} .

TABLE 4. Thermal Properties of Polyesters

Polymer sample	Temperature (°C) for various % decompositions				
	10	20	30	40	50
IV _a	285	300	310	325	330
IV _b	255	305	315	335	340
IV _c	285	330	360	365	370
IV _d	270	300	330	365	390
IV _e	280	305	315	340	395
IV _f	300	310	325	365	295
V _a	265	285	320	360	390
V _b	250	280	315	255	380
V _c	280	310	335	365	385
V _d	265	270	275	300	335
V _e	275	295	325	345	390
V _f	290	315	330	370	400

The thermal behavior of polyesters IV_{a-f} and V_{a-f} was evaluated by differential scanning calorimetry (DSC), DTA, and thermogravimetric analysis (TGA) in air. TG curves of polymers IV_{a-f} and V_{a-f} are given in Figs. 5 and 6. Table 4 gives the temperatures for various percentage weight losses. All the polymers showed similar decomposition patterns. The temperature for a 10% weight loss is considered to be the polymer decomposition temperature, and it ranges between 250 and 300°C. Comparison of the T_{10} values of the polyesters derived from isophthaloyl (IV_b, V_b) were somewhat less thermally stable than the other polyesters. The polyesters derived from the monomeric unit of 2,5-bis(4-hydroxybenzylidene)cyclopentanone are more thermally stable than the polyesters derived from 2,5-bis(4-hydroxy-3-methoxy)cyclopentanone. In particular, the polymer-based aliphatic (IV_f and V_f) in Table 4 showed elevated T_{10} values, and that may be attributed to the high degree of crystallinity of these polymers.

The electrical conductivity of the synthesized polyesters IV_{a-f} and V_{a-f} were examined and gave values in the 10^{-13} to 10^{-15} (ohm·cm)⁻¹ range. This indicates that the polymers are possible insulator materials (Table 1).

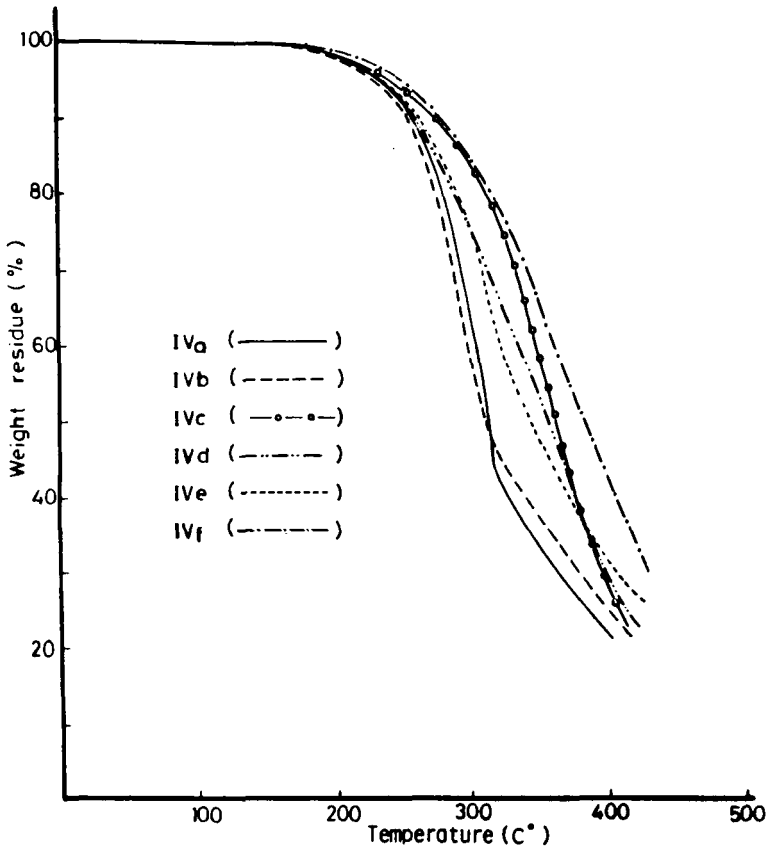


FIG. 5. Thermogravimetric curves of polyesters IV_{a-f}.

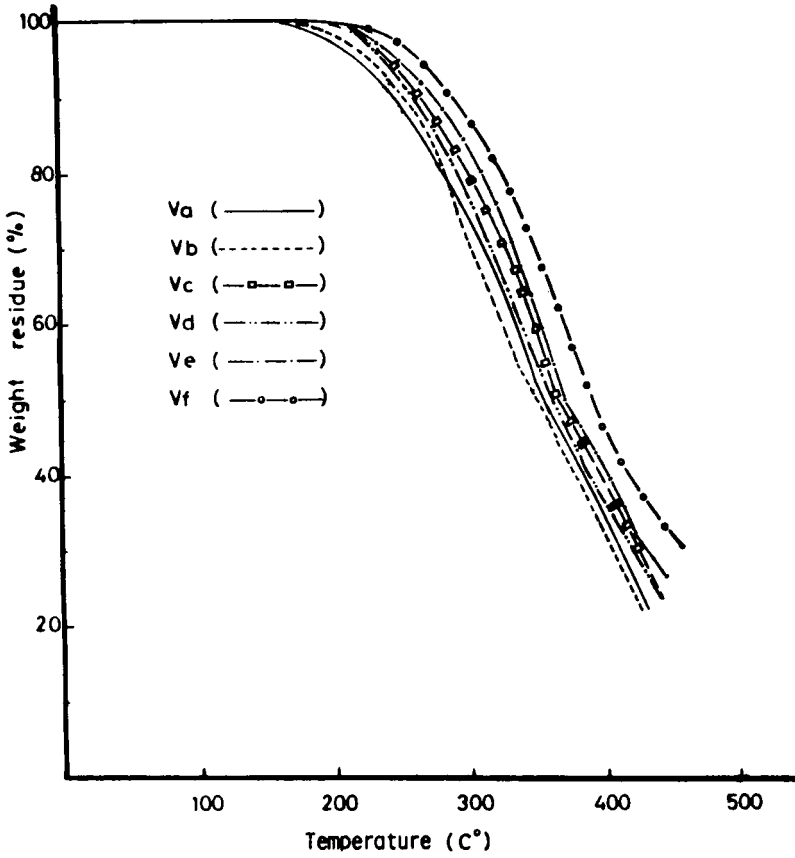


FIG. 6. Thermogravimetric curves of polyesters V_{a-f}.

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